

Design of a Pharmaceutical and Personal Care Product Project for the City of Dallas, Texas 2009-2013

By Mick Baldys

In cooperation with Dallas Water Utilities

Red River Basin – Advisory
Committee Meeting, Wichita
Falls, March 29, 2011

What Are “Emerging Contaminants”?



- Emerging contaminants (“ECs”) are organic compounds including: hormones, food additives, detergents, and pharmaceuticals that typically occur in parts-per-trillion or parts-per-billion concentrations in water.
- These contaminants are called “emerging” because methods for their analyses are experimental and analytical method development is on-going.
- The health effects to humans and biota from long-term exposure to small concentrations are unknown.

Human-Use Pharmaceuticals

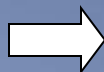
- **Extremely little is known about the effects of these substances on non-target organisms, many of which have different metabolic pathways and different potential receptors.**
- **By their nature, pharmaceuticals are designed to be highly bioactive -- many exquisitely so.**
- **What little that is known serves to show that rather low concentrations at least have the potential to exert substantive effects on aquatic life."**

Christian Daughton, Ph.D.

U.S. EPA, Office of Research & Development

Sources of Emerging Contaminants

- Agriculture
- WWTPs
- Domestic septic systems
- Industrial discharges (medical)
- Illicit drugs



Target Compounds - Antibiotics

Tetracyclines

Anhydrochlorotetracycline
Anhydrotetracycline
Chlorotetracycline
Demeclocycline
Doxycycline
Minocycline
Oxytetracycline
Tetracycline

Quinolones

Ciprofloxacin
Clinafloxacin
Flumequine
Lomefloxacin
Norfloxacin
Ofloxacin
Oxolinic acid
Sarafloxacin

Beta Lactams

Amoxicillin
Ampicillin
Cefotaxime

Sulfonamides

Sulfachloropyridazine
Sulfadiazine
Sulfadimethoxine
Sulfamerazine
Sulfamethazine
Sulfamethoxazole
Sulfathiazole

Macrolides

Anhydroerythromycin
Erythromycin
Lincomycin
Ormetoprim
Roxithromycin
Trimethoprim
Tylosin
Virginiamycin

Beta Lactams – cont.

Cloxacillin
Oxacillin
Penicillin G
Penicillin V

Target Compounds - Human Prescription and Nonprescription Drugs

Prescription

Carbamazepine (anticonvulsant)
Cimetidine (antacid)
Codeine (analgesic)
Diltiazem (antihypertensive)
Diphenhydramine (antihistamine)
Fluoxetine (antidepressant)
Furosemide (diuretic)
Gemfibrozil (antihyperlipidemic)
Miconazole (antifungal)
Salbutamol (asthmatic)
Sulfamethoxazole (antibiotic)
Thiabendazole (fungicide)
Trimethoprim (antibiotic)
Warfarin (anticoagulant)

Non-prescription and Metabolites

1,7-dimethylxanthine (caffeine metabolite)
Acetaminophen (antipyretic)
Caffeine (stimulant)
Cotinine (nicotine metabolite)
Dehydronifedipine (nifedipine metabolite)
Digoxigenin (digoxin metabolite)
Ibuprofen (antiinflammatory)
Ranitidine (antacid)

Target Compounds – Industrial and Household-use Chemicals

Fragrances and Flavorants

AHTN
HHCB
3-Methyl-1H-indole (skatol)
Acetophenone
Camphor
Isoborneol
Isoquinoline
Menthol

Flame Retardants

Tris(2-chloroethyl) phosphate
Tris(dichlorisopropyl) phosphate
Tributyl phosphate

Antioxidants

5-Methyl-1H-benzotriazole
3-*tert*-butyl-4-hydroxyanisole (BHA)

Fuel-Related Compounds

1-Methylnaphthalene
2,6-Dimethylnaphthalene
2-Methylnaphthalene
Isopropylbenzene (cumene)

Detergent Metabolites

p-Cumylphenol
p-n-Octylphenol
p-Nonylphenol diethoxylate (NPEO2)
p-Octylphenol diethoxylate (OPEO2)
p-Octylphenol monoethoxylate (OPEO1)
p-tert-octylphenol
p-Nonylphenol (total, NP)

Plasticizers

Bisphenol A
Tris(2-butoxyethyl) phosphate
Triphenyl phosphate

Disinfectants

Triclosan

Phenol

Solvents and Preservatives

Isophorone

Tetrachloroethylene

p-cresol

Pentachlorophenol

Target Compounds – Industrial and Household-use Chemicals (Cont.)

Pesticides

Bromacil

Carbaryl

Carbazole

Chlorpyrifos

Diazinon

d-Dichlorvos

d-Limonene

Indole

Metalaxyl

Metolachlor

N,N-diethyl-meta-toluamide (DEET)

Prometon

Plant and Animal Steroids

3- β -coprostanol

β -sitosterol

β -stigmastanol

Cholesterol

PAHs

Anthracene

Benzo[a]pyrene

Fluoranthene

Naphthalene

Phenanthrene

Pyrene

Others

Anthraquinone (manufacturing)

1,4-dichlorobenzene (deodorizer)

Benzophenone (fixative)

Bromoform (disinfection byproduct)

Caffeine (stimulant)

Cotinine (nicotine metabolite)

Methyl salicylate (liniment)

Triethyl citrate (ethyl citrate) (cosmetics)

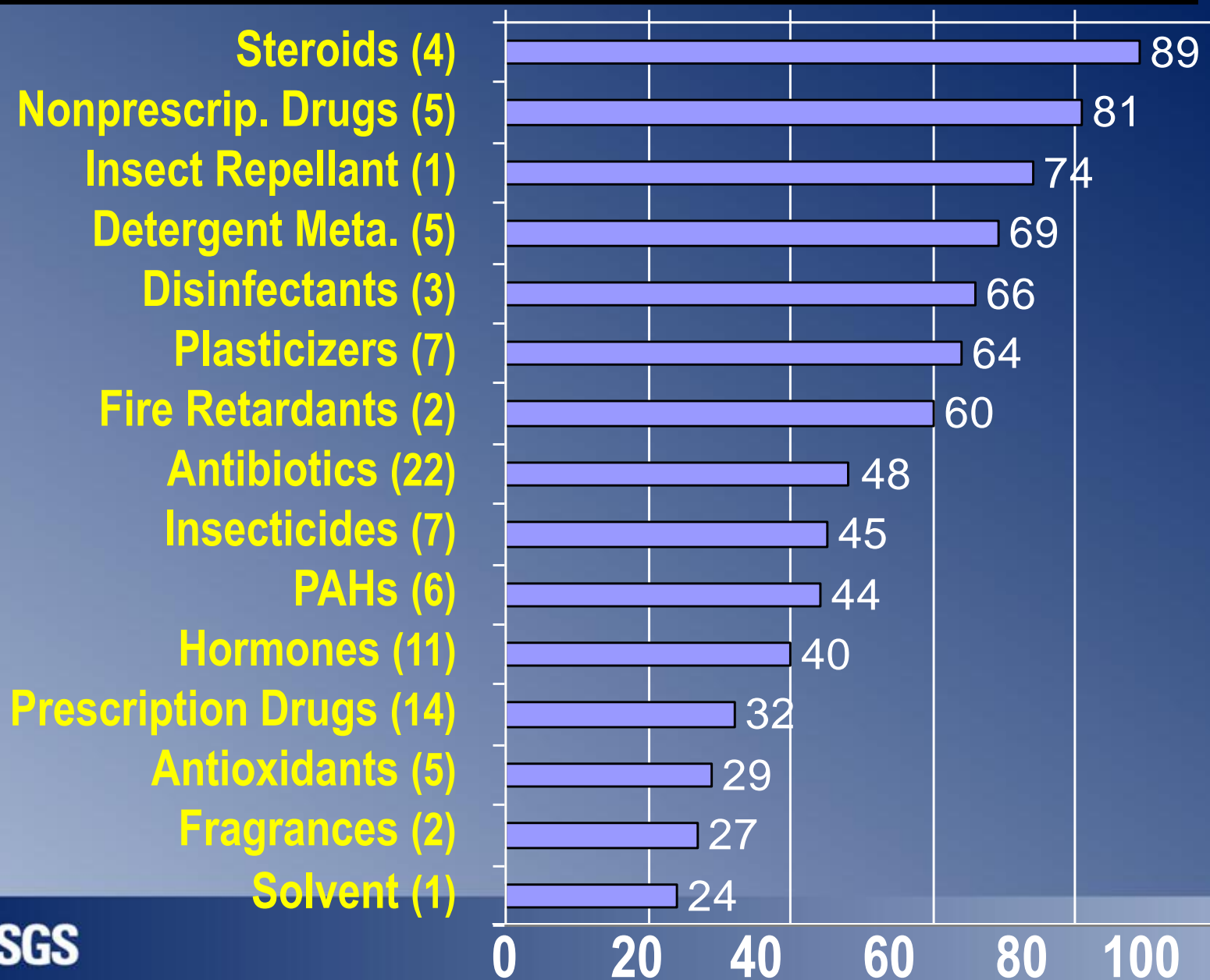
Occurrence

The first step in the road to understanding the fate of a contaminant is determining if contamination is actually taking place.

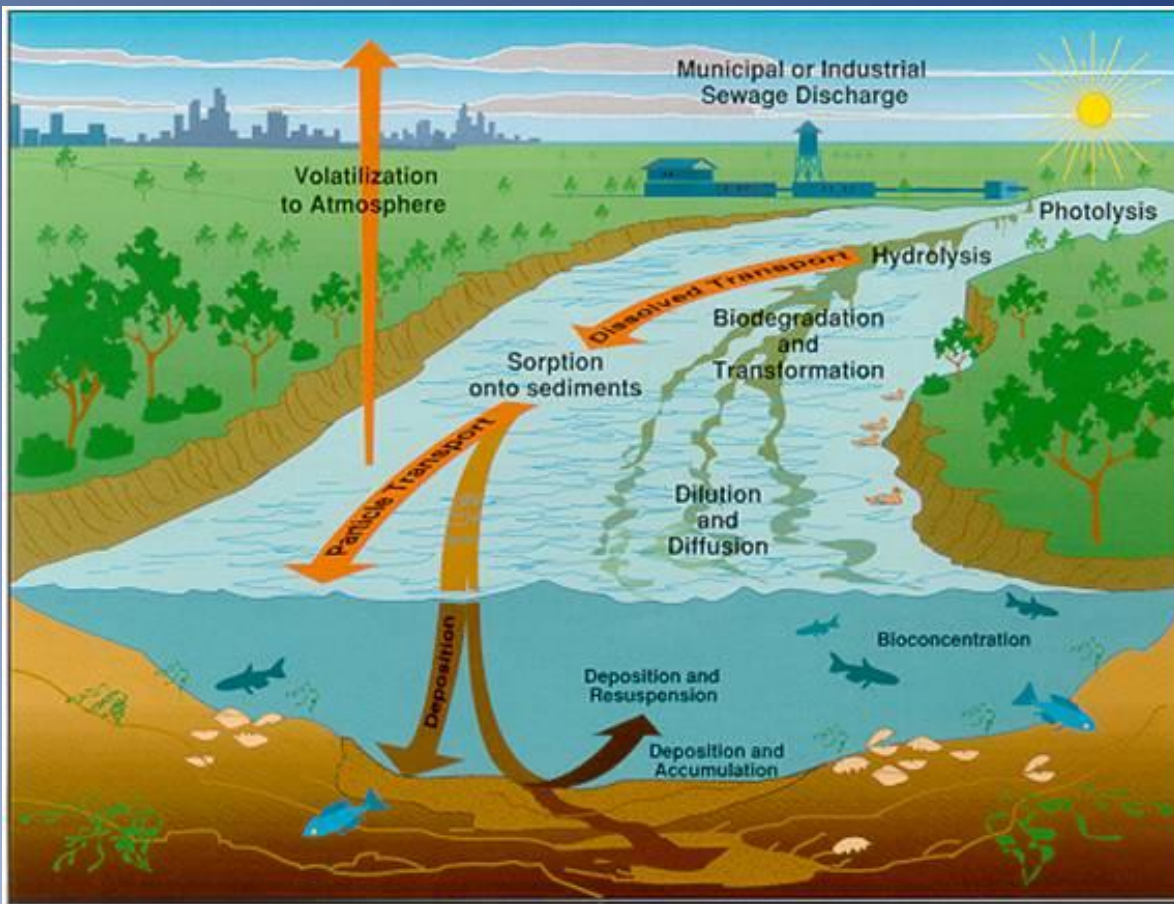


- What compounds enter the environment?
- At what levels do they occur?
- In what mixtures do they occur?

Detection Frequency (%) by Group (National Study)



Transport and Fate



In order to minimize ecologic effects, it is essential to understand how a contaminant moves and is altered in the environment.

(Barber and others, 1995)

Dallas, Texas



Objectives of the study

Objectives: The objectives of this study are to determine the occurrence, distribution and concentration of pharmaceutical compounds and personal care products for the City of Dallas in :

1. Raw and treated potable water
2. Raw and treated wastewater
3. Trinity River, in both the water column and the channel bottom sediments from Dallas to Trinidad, Tex.

Major chemical groupings

(number of constituents in grouping)

- Wastewater compounds (65)
- Human health pharmaceuticals (16)
- Sex hormones and steroids (27)
- Hormones in filtered waters (30)
- Wastewater compounds in sediment (60)

City of Dallas Pharmaceutical and Personal Care Product Study

Pharmaceutical and Personal Care Products Project Workplan				
	2009	2010	2011	2012
Work Item	A M J J A S	O N D J F M A M J J A S	O N D J F M A M J J A S	O N D J F M A M J J A S
Potable water plant sampling	X	X X X X X		X
Wastewater treatment plant sampling	X	X X X	X X	
Main stem Trinity River Sites	X	X	X X X	X
Equipment Blank	X X	X	X X	X
Quality Assurance/Control water matrix	X	X X X	X	
Quality Assurance/Control sediment matrix	X		X	
Update Cooperator	X	X X X	X X X	X X X X
Data Analysis and report preparation			XXXXXXXXXXXXX	XXXXXXXXXXXXX
Report to cooperator				X

Safety

- Minimize exposure to and effects from contaminated water, as described in the USGS National Field Manual (NFM) 9.7.
- Receive proper immunizations before engaging in field activities.
- Avoid direct contact with sewage and other types of wastewater and with equipment still contaminated through contact with the sample or source water by using appropriate personal protective equipment and decontamination procedures.
- Avoid breathing in sewage and wastewater fumes or mist.
- Do not use workspace surfaces or equipment that has come into contact with polluted water until they have been decontaminated. Use only those decontamination procedures that are described in the USGS NFM 9.7 under “Prevent sample contamination”.

Quality Assurance and quality control samples

- Equipment Blanks
 - Replicates
 - Field Blanks
 - Surrogates

Sample Handling Protocols

On the day of sampling activities, avoid contact with or consumption of the following products:

Wastewater compounds:

- Soaps and detergents, including antibacterial cleansers
- DEET (active ingredient in most insect repellents)
- Fragrances (cologne, aftershave, perfume)
- Sunscreen
- Animal or human urine or excrement
- Caffeine (coffee, tea, colas)
- Tobacco

Sample Handling Protocols

Pharmaceutical compounds:

- Prescription drugs, medications, and hormonal substances
- Over-the-counter medications
- Selected human antibiotics
- Veterinary antibiotics

Sampling Equipment

- Select sampling and processing equipment made of fluorocarbon polymers, glass, aluminum, or stainless steel.
- Avoid equipment made of Tygon, polyethylene, or other plastics.
- Clean equipment thoroughly before use, following the general protocols for organic-compound samples



City of Dallas Treatment Plants

Three Potable water treatment plants

Two Wastewater treatment plants

-

Potable Water Treatment Plant

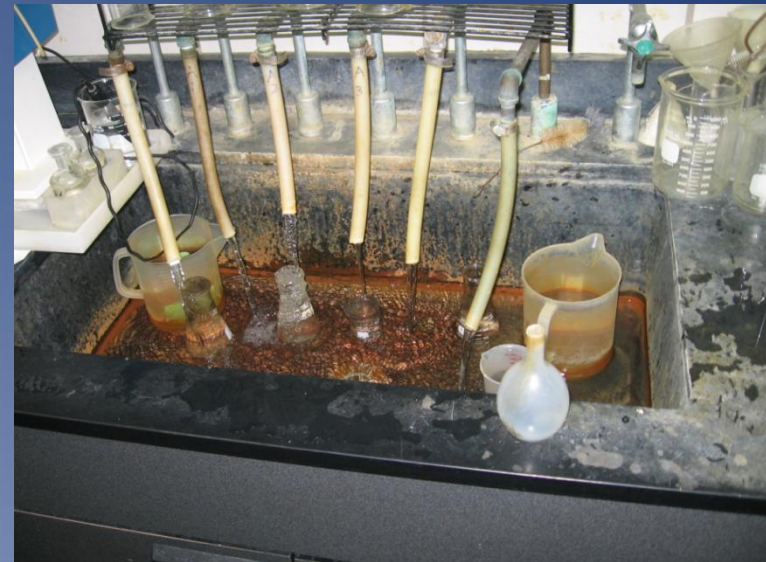


Inflow



Raw water
sampling point

Finished
water
sampling
point





Raw water sampling point



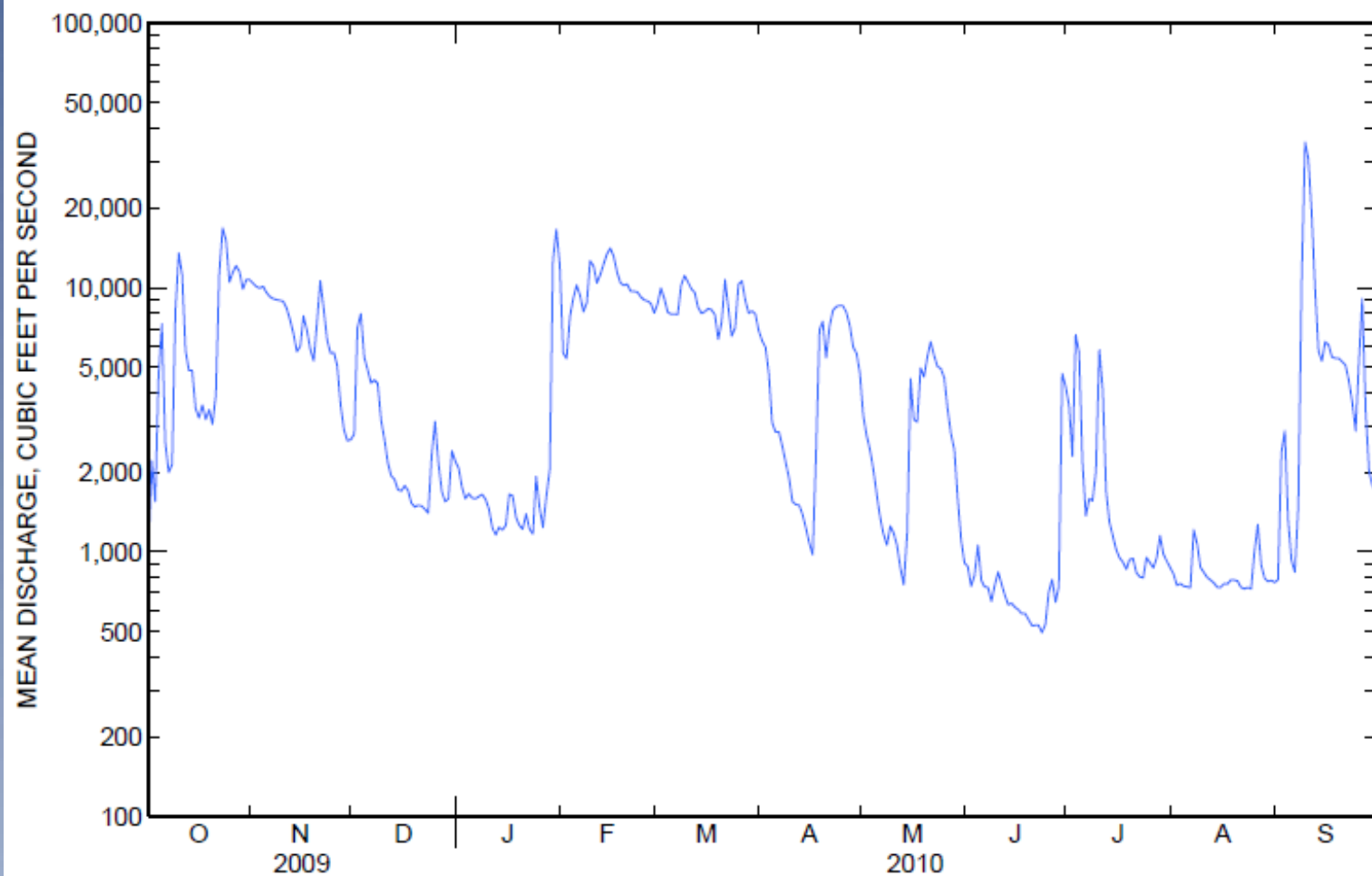
Finished water sampling point



**Wastewater
Treatment Plant**

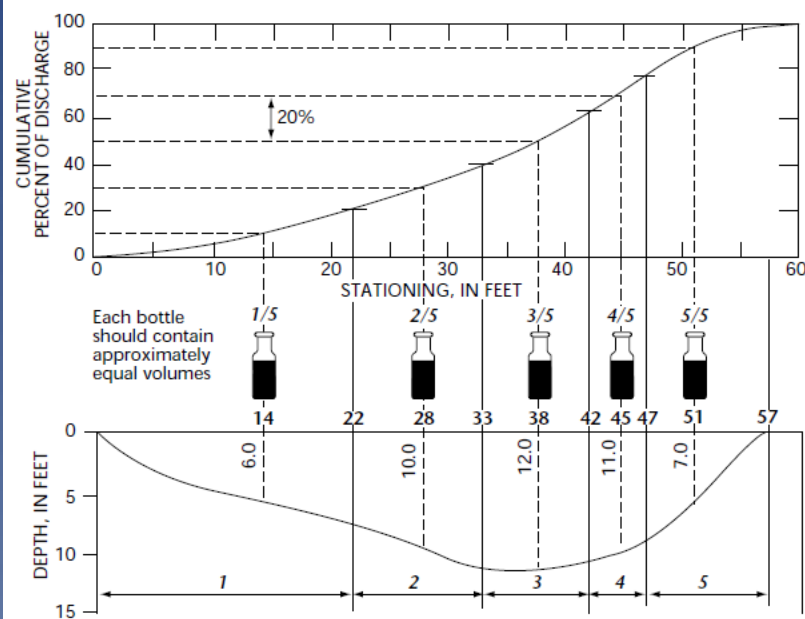


08057410 Trinity River Below Dallas, TX 2010 Water Year



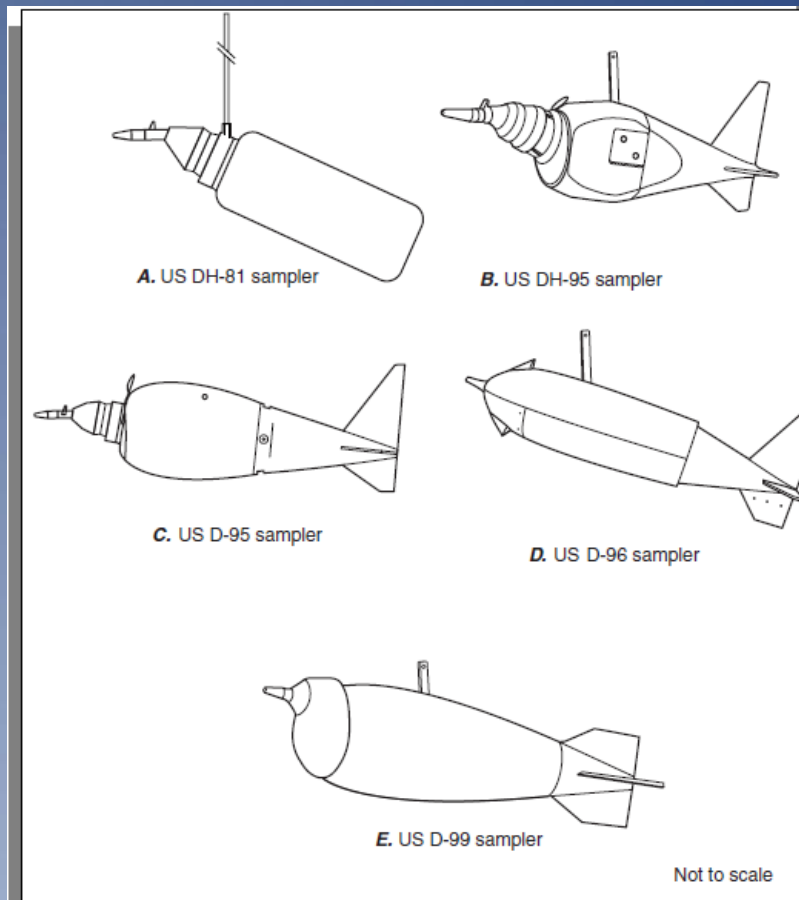
Equal Discharge Increment (EDI) Sampling

Example: Sampler D77; nozzle size, 5/16 inches ID; 3 Liter sample bottle; width 57 feet; maximum depth 12 feet; maximum velocity, 5.0 ft/s; width of section containing 20 percent of flow is variable, 5 to 22 feet; 20 percent of flow per section will give 5 sampling verticals; transit rate variable, 0.3 to 1.7 ft/s.



Sampling vertical bottle/ number	Percent discharge	Increment centroid from left edge of water, in feet	Increment depth, in feet	Velocity, in feet per second	Transit rate to give 2.7 liters, in feet per second
1/5	20	14	6	2.5	0.16
2/5	20	28	10	3.0	.33
3/5	20	38	12	3.1	.41
4/5	20	45	11	6.1	.72
5/5	20	51	7	4.8	.37

Depth Integrating Sampler and Fluoropolymer Churn Splitter



Bed material sampling equipment



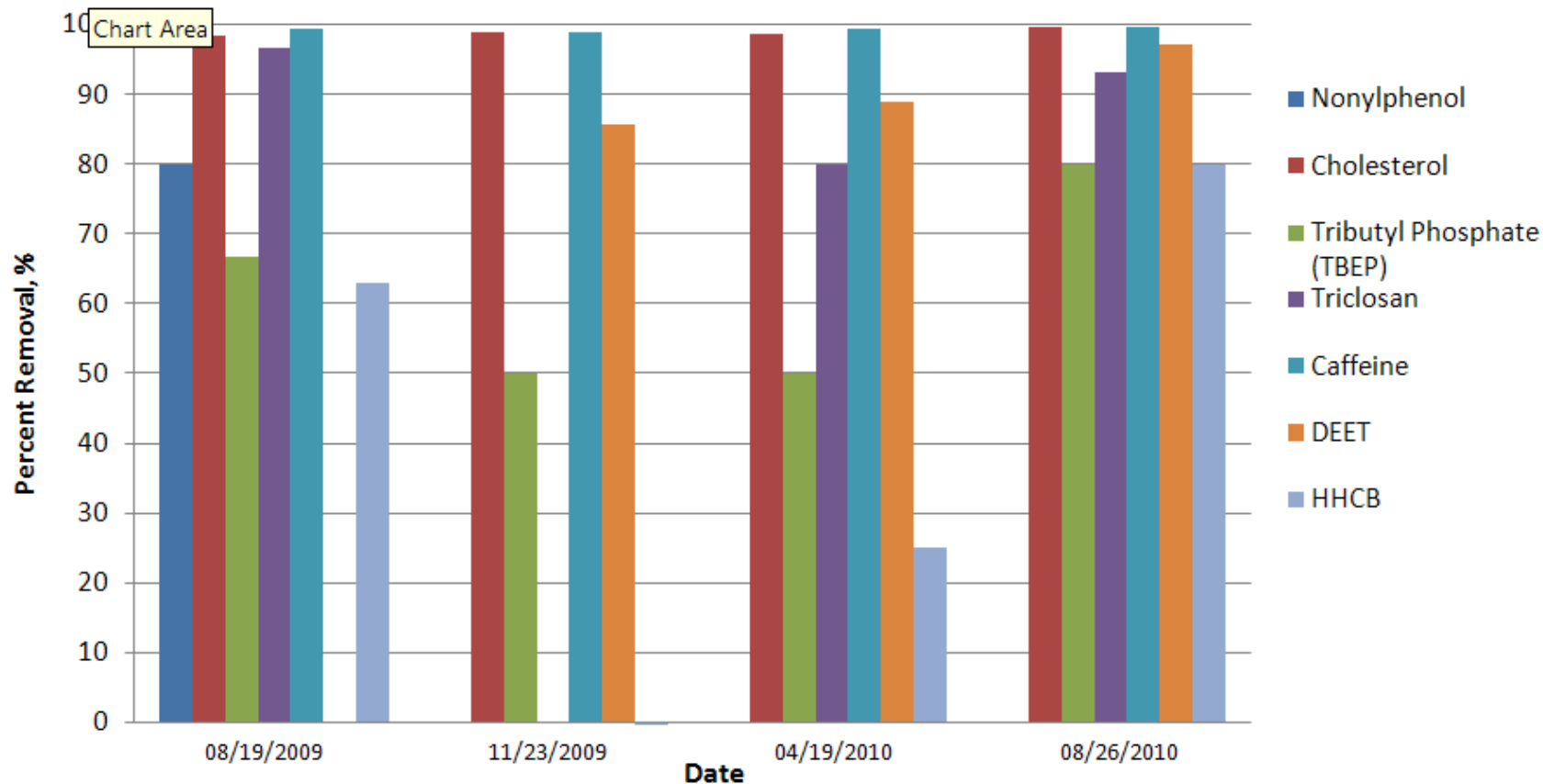
Constituents of Concern

- Carbamazepine: is used to control seizures caused by certain types of epilepsy
- Cotinine: Cotinine is used as a biomarker for exposure to tobacco smoke and has also been sold as an antidepressant under the brand name *Scotine*.
- Triclosan: toothpastes, deodorants, shaving creams
- Fryol FR2: flame retardant

Constituents of concern take two!

- HHCB: ingredient in commercial preparations intended to be used as fragrances in a wide variety of consumer products such as perfumes, cosmetics, household and laundry cleaning products and air fresheners
- DEET(N,N-Diethyl-meta-toluamide): insect repellent
- Caffeine: necessary stimulant (especially in morning)... psychoactive substance

WWTP - Percent Removals of Emerging Contaminants



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And Many Others.....

The Toxics Program:

toxics.usgs.gov

FLASHBACK



LEWIS/GETTMAN

■ FROM THE GEOGRAPHIC ARCHIVES

An ill wind

A cloud of the insecticide DDT billows over the beach—and beachgoers—in 1945 as part of a mosquito-control program at New York's Jones Beach State Park. Used in Europe to ward off bug-borne disease during World War II, DDT was once hailed as a miracle product. This photograph was published in the October 1945 *GEOGRAPHIC* article "Your New World of Tomorrow." But by the time "tomorrow" came, evidence showed that birds from sprayed areas accumulated high levels of DDT, damaging their ability to reproduce. Other research pointed to the chemical as a human carcinogen. Use of DDT was banned in the United States in 1972.



Questions????



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